

30 Space-group corrections: two examples of false polymorphism and one of incorrect interpretation of the fine details of an IR spectrum

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Revised structures are reported for 30 crystalline compounds, based on space groups of higher symmetry than originally reported. In 18 cases the Laue class is revised, in seven cases the center of symmetry is added, in two cases the Laue class change is coupled with the addition of the center of symmetry, in two cases the addition of the center of symmetry also requires the addition of systematic absences and, finally, one case of the addition of systematic absences without changing the Laue group is reported. Two examples (CSD refcodes: DAMLIM and ABPZCU01) of false polymorphism and one (PAVJUR) of the erroneous interpretation of the fine details of IR spectra, owing to incorrect space-group determination, have been detected.

1. Introduction

The number of published structural studies described in space groups of unnecessarily low symmetry is exponentially growing and approximately 800 structures have so far been corrected and reported in the CSD (Cambridge Structural Database, version 5.24, November 2002, ~ 272 000 entries; Allen, 2002). See *Appendix A* for a more detailed discussion about this point. The decrease in symmetry produces unrealistic bond lengths and angles when a centre of symmetry goes unrecognized or when a non-space-group translation is introduced in the structure (Schomaker & Marsh, 1979). In the other cases, the reported molecular structure is essentially correct (error ~ 0.02–0.04 Å), but two important errors, besides those already reported (Marsh, 1995; Clemente & Marzotto, 2003), may be introduced:

(i) the incorrect attribution of polymorphism due to an incorrect space-group determination. We have described here two examples: the pairs of crystal structures with CSD refcodes DAMLIM and DAMLIM01, and ABPZCU and ABPZCU01.

(ii) an incorrect interpretation of the fine details of the IR or NMR spectra owing to the apparent presence of two purportedly independent molecules in the asymmetric unit with apparently slightly different crystal environments.

The crystal structures pertaining to CSD refcodes BIHJUX, BIHLIN, FARNER and FARNIV (Clemente & Marzotto, 2003) are already reported examples and now we add the structure PAVJUR. We believe that these errors are rather

common in the literature and its number is proportional to the time spent searching for them.

2. Data retrieval and methods

Throughout this paper crystal structures will be referred to by the six-letter (or six-letter + two-digit) refcode assigned in the CSD. The chemical identity of each compound can be found in Table 1. The coordinates were obtained from the above-mentioned version of the CSD, which we follow for the numbering of atoms. Mostly we have used the classification of space-group changes suggested by Marsh *et al.* (2002). However, we have added two new categories: C for GEWLEZ and YAXKOX and E for QUIXKEY (see Table 1). The new crystal systems are described following the conventions proposed by Mighell (2003).

PLATON/ADDSYM (Marsh & Spek, 2001) is the principal program used to find the space-group changes but, since this program always gives a C-centered monoclinic cell or the space group $P2_1/c$, the programs written by us (Clemente & Marzotto, 2003) were used in all the other cases. It was possible to obtain a list of observed structure factors for AZCDCO, PAJVUR and WERBIE, and the structures were re-refined in the revised space group. Standard deviations on intensities were assigned according to $\sigma^2(I) = I + (pI)^2$ with $p = 0.04$ (Rees, 1977). Full-matrix refinements were carried out using SHELXL97 (Sheldrick, 1997).

Table 1 summarizes the 30 space-group changes, the original and revised crystallographically imposed molecular symmetry and the principal geometry corrections. Revised crystal data are appended as deposited CIFs and have been submitted to the CSD. A few entries in Table 1 deserve special note; a complete detailed discussion for all the compounds is deposited as supplementary materials.¹

3. Category A: change in Laue group

3.1. ABPZCU01: *cis*-diaqua-(2,2-bipyridyl-*N,N'*)-copper sulfate, triclinic polymorph, $[\text{C}_{10}\text{H}_{12}\text{CuN}_2\text{O}_2]^{2+} \cdot \text{SO}_4^{2-}$ (Chattopadhyay & Mak, 2000)

This structure was reported in the space group $P\bar{1}$ (No. 2), $Z = 2$. The triclinic cell can be transformed to the *I*-body centered cell, space group $I2/a$ (No. 15), with $a = 6.963$, $b = 12.469$, $c = 14.854$ Å, $\alpha = 89.95$, $\beta = 101.01$, $\gamma = 90.30^\circ$, $Z = 4$. The transformation matrix is $(100, 01\bar{1}, 111)$. The $[\text{Cu}(2,2\text{-bipy})_2(\text{OH}_2)_2]^{2+}$ cation now lies on a twofold axis along b and the same is true for the SO_4^{2-} anion. Moreover, the transformation matrix $(01\bar{1}, 01\bar{1}, 100)$ leads to a C-centered cell, space group $C2/c$, with $a = 15.152$, $b = 12.469$, $c = 6.963$ Å, $\alpha = 90.30$, $\beta = 105.80$, $\gamma = 89.91^\circ$. This C-centered cell immediately reveals that the claimed triclinic polymorph is in fact the already known ABPZCU (Tedenac *et al.*, 1976).

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS0022). Services for accessing these data are described at the back of the journal.

3.2. AZCDCO: dinitro-(1,4,7,10-tetra-azacyclododecane)-cobalt(III) chloride monohydrate, $[\text{C}_8\text{H}_{20}\text{CoN}_6\text{O}_4]^+ \cdot \text{Cl}^- \cdot \text{H}_2\text{O}$ (Iitaka *et al.*, 1974)

This cobalt(III) complex was reported in the space group $P2_1$ (No. 4), $Z = 2$. Transforming the axes by the lattice vectors $[101]$, $[\bar{1}01]$, $[01\bar{0}]$ and shifting the origin to $(-1/4, 1/4, 0)$ gives a C-centered cell, space group $Cmc2_1$ (No. 36), with the dimensions: $a = 9.515$, $b = 11.909$, $c = 13.003$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 90.08^\circ$, $Z = 4$. The cation now possesses an exact mirror plane, passing through Co1, N4, N10, N13, N16, O19 water oxygen and the Cl1 anion, and not only an approximate mirror plane as the original authors reported. 1148 F_o values were taken from the supplementary material of *Inorg. Chem.* and were averaged according to Laue symmetry *mmm*; $R(\text{int})$ (on I) was 0.037 for 491 pairs of equivalent reflections; the total number of independent reflections in $Cmc2_1$ was 654. The new space group requires the additional reflection condition $(h,0,l)$ to be absent for $l(h)$ odd; in the monoclinic setting this condition becomes (h,k,h) being absent for k odd. Only two reflections of this type are present, one (131) is reported as unobserved by the original authors, while the other (474) has $F_o = 15$, which is four times the threshold value. All non-H atoms were refined with anisotropic thermal parameters and H atoms were included in calculated positions. The final $[R(F)]$ index was 0.030 $[(R(F)) = \sum||F_o| - |F_c||/\sum|F_o|]$, for all the 654 reflections and 118 variables. The $[R(F)]$ index obtained by the previous authors was 0.026, but for 277 parameters. Since $Cmc2_1$ contains mirror and glide planes, the original authors' discussion of absolute configuration is irrelevant.

3.3. DAMLIM: (*R*,R**)-4,4'-bi(1-*tert*-butylcyclohexen-3-one), triclinic polymorph, $\text{C}_{20}\text{H}_{30}\text{O}_2$ (Arain *et al.*, 1985)

This compound was reported as being triclinic (see the supplementary material or the CSD file), space group $P\bar{1}$ (No. 2), $Z = 2$. Transforming the axes by $[112]$, $[100]$, $[01\bar{0}]$ gives an *I*-centered cell, space group $I2/a$ (No. 15), with the dimensions: $a = 27.869$, $b = 5.771$, $c = 11.758$ Å, $\alpha = 90.02$, $\beta = 91.43$, $\gamma = 90.01^\circ$. The molecule now lies on a twofold axis passing between C1 and C7. The bond distances remain unchanged. Three years later the same authors (Arain *et al.*, 1988) published the same compound, but in the space group $C2/c$, thus the CCDC has archived it as the monoclinic polymorph with the refcode DAMLIM01. However, the lattice vectors $[10\bar{2}]$, $[\bar{1}00]$, $[010]$ transform the triclinic polymorph DAMLIM into the monoclinic polymorph DAMLIM01.

3.4. PAJVUR: *trans*-(1,4,8,11-tetra-azacyclotetradecane)-dioxorhenium hexafluorophosphate, $[\text{C}_{10}\text{H}_{24}\text{N}_4\text{O}_2\text{Re}]^+ \cdot (\text{PF}_6)^-$ (Luna *et al.*, 1992)

The structure of this complex, *trans*- $[\text{ReO}_2(\text{cyclam})]^+(\text{PF}_6)^-$, was reported as being triclinic, space group $P\bar{1}$ (No. 2), but it can be better described as the monoclinic space group $I2/a$ (No. 15). The transformation matrix $[\bar{1}11]$, $[100]$, $[011]$ defines a monoclinic cell with $a = 17.257$, $b = 5.533$, $c = 18.053$ Å, $\alpha = 89.94$, $\beta = 98.14$, $\gamma = 90.01^\circ$.

Table 1

Structures originally described in space groups which should be described in higher symmetries.

When there is more than one residue in the asymmetric unit, only the most populated residue is analysed. The corrections have been ordered by Category and then by refcode (alphabetically). The original and revised space groups are both included in the table. The shifts necessary to achieve the higher symmetry are defined as one half of the distance between the two (now) equivalent atoms when they are brought as near as possible to each other by the added symmetry elements. Only the shifts of the non-H atoms are reported. In the column labelled TMD the two most disparate chemically equivalent distances in the lower symmetry group and the corresponding value in the higher symmetry group are reported.

| Number | Refcode | Formula unit | Original space group | Revised space group | Original crystallographically imposed molecular symmetry | Revised crystallographically imposed molecular symmetry | Atomic shifts ($\times 10^3$ Å) min \leftrightarrow max | TMD (Å) |
|---|----------|--|------------------------------------|---|--|---|---|---|
| Category A: Change in Laue group | | | | | | | | |
| 1 ^a | ABPZCU01 | [C ₁₀ H ₁₂ CuN ₂ O ₂] ²⁺ ·SO ₄ ²⁻ | <i>P</i> $\bar{1}$ | <i>I</i> 2/ <i>a</i> | 1 | 2 | 2 \leftrightarrow 7 | C—C 1.378 \leftrightarrow 1.392 \rightarrow 1.385 |
| 2 ^b | AZDCDO | [C ₈ H ₂₀ CoN ₆ O ₄] ⁺ ·Cl ⁻ ·H ₂ O | <i>P</i> 2 ₁ | <i>C</i> <i>m</i> c2 ₁ | 1 | <i>m</i> | 5 \leftrightarrow 10 | C—C 1.508 \leftrightarrow 1.528 \rightarrow 1.515 |
| 3 ^c | BETWUS | C ₂₃ H ₃₉ N ₅ O ₄ Si ₂ | <i>P</i> 2 ₁ | <i>C</i> 222 ₁ | 1 | 1 | 0 \leftrightarrow 41 | C—C 1.515 \leftrightarrow 1.551 \rightarrow 1.533 |
| 4 ^d | DAMLIM | C ₂₀ H ₃₀ O ₂ | <i>P</i> $\bar{1}$ | <i>I</i> 2/ <i>a</i> | 1 | 2 | 3 \leftrightarrow 17 | C—C 1.527 \leftrightarrow 1.554 \rightarrow 1.541 |
| 5 ^e | FAXPID | [C ₂₃ H ₃₂ ClCuN ₄] ⁺ ·Cl ⁻ ·H ₂ O | <i>P</i> $\bar{1}$ | <i>I</i> 2/ <i>a</i> | 1 | 1 | 1 \leftrightarrow 16 | C—C 1.331 \leftrightarrow 1.363 \rightarrow 1.351 |
| 6 ^f | GADFOG | 2C ₁₆ H ₁₇ N ₂ O ₅ S ⁻ ·Ca ²⁺ ·2H ₂ O | <i>P</i> 2 ₁ | <i>C</i> 222 ₁ | 1 | 2 | 3 \leftrightarrow 83 | C—C 1.300 \leftrightarrow 1.443 \rightarrow 1.370 |
| 7 ^g | GOHPAU | [C ₁₂ N ₈ MY ₂] ⁻ ·[C ₇ H ₁₈ N] ⁺ · CH ₃ CN (<i>M</i> = 2/3Ir, 1/3Pt; <i>Y</i> = 2/3O, 1/3N) | <i>P</i> 2 ₁ | <i>C</i> <i>m</i> c2 ₁ or <i>C</i> <i>m</i> <i>c</i> <i>m</i> | 1 | <i>m</i> or <i>m</i> 2 <i>m</i> | 7 \leftrightarrow 47 | C—C 1.337 \leftrightarrow 1.395 \rightarrow 1.365 |
| 8 ^h | GULDOG | C ₁₃ H ₁₂ ClNO ₄ | <i>P</i> 2 ₁ / <i>c</i> | <i>C</i> <i>m</i> <i>c</i> <i>a</i> | 1 | <i>m</i> | 0 \leftrightarrow 11 | — |
| 9 ⁱ | HOPFUN | C ₁₀ H ₁₂ N ₄ O ₈ P·9H ₂ O | <i>P</i> 2 ₁ | <i>C</i> 222 ₁ | 1 | 1 | 2 \leftrightarrow 25 | C—N 1.332 \leftrightarrow 1.388 \rightarrow 1.360 |
| 10 ^j | NEJBAF | (C ₁₈ H ₂₂ N ₂ O ₈ Zn ₂) _{<i>n</i>} | <i>P</i> $\bar{1}$ | <i>P</i> 2 ₁ / <i>n</i> | 1 | 1 | 0 \leftrightarrow 41 | C—C 1.44 \leftrightarrow 1.52 \rightarrow 1.48 |
| 11 ^j | NEJBOT | [C ₁₀ H ₁₈ FeN ₂ O ₄] ²⁺ ·2(C ₂ H ₃ O ₂) ⁻ | <i>P</i> $\bar{1}$ | <i>I</i> 2/ <i>m</i> | $\bar{1}$ | 2/ <i>m</i> | 2 \leftrightarrow 3 | C—N 1.321 \leftrightarrow 1.327 \rightarrow 1.324 |
| 12 ^k | PAJVUR | [C ₁₀ H ₂₄ N ₄ O ₂ Re ^V] ⁺ ·PF ₆ ⁻ | <i>P</i> $\bar{1}$ | <i>I</i> 2/ <i>a</i> | $\bar{1}$ | $\bar{1}$ | 0 \leftrightarrow 25 | C—N 1.47 \leftrightarrow 1.56 \rightarrow 1.50 |
| 13 ^l | POFXUD | C ₆₀ H ₁₂₀ Fe ₆ N ₁₂ O ₂₄ | <i>C</i> 2/ <i>c</i> | <i>C</i> <i>c</i> <i>c</i> <i>a</i> | 2 | 222 | 0 \leftrightarrow 61 | C—C 1.45 \leftrightarrow 1.55 \rightarrow 1.50 |
| 14 ^m | QIPBEW | C ₉₆ H ₈₀ P ₄ Pd·2C ₆ H ₆ | <i>P</i> 2 ₁ | <i>C</i> 222 ₁ | 1 | 2 | 1 \leftrightarrow 86 | C—C 1.38 \leftrightarrow 1.42 \rightarrow 1.40 |
| 15 ⁿ | WERBIE | C ₁₉ H ₂₂ Cl ₂ CuN ₆ O ₅ S ₄ | <i>P</i> $\bar{1}$ | <i>I</i> 2/ <i>a</i> | 1 | 2 | 0 \leftrightarrow 68 | S—C 1.729 \leftrightarrow 1.745 \rightarrow 1.710 |
| 16 ^o | WOHFOO | (C ₂₈ H ₂₈ Cd ₂ N ₄ O ₁₄) _{<i>n</i>} ·4 <i>n</i> (H ₂ O) | <i>P</i> $\bar{1}$ | <i>C</i> 2/ <i>c</i> | 1 | 2 | 0 \leftrightarrow 5 | C—C 1.384 \leftrightarrow 1.390 \rightarrow 1.387 |
| 17 ^p | XATYOG | C ₂₀ H ₁₅ FeNO ₂ | <i>P</i> $\bar{1}$ | <i>P</i> 2 ₁ / <i>n</i> | 1 | 1 | 0 \leftrightarrow 6 | C—O 1.390 \leftrightarrow 1.398 \rightarrow 1.394 |
| 18 ^q | ZOSLIC | $\frac{1}{2}$ [C ₁₀ H ₂₄ Cl ₂ Mg ₂ O ₈] ²⁺ · $\frac{1}{2}$ [C ₁₀ H ₂₀ MgO ₆] ²⁺ ·2Cl ⁻ | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> <i>m</i> <i>n</i> <i>a</i> | 1 | 2/ <i>m</i> | 3 \leftrightarrow 124 [†] | Mg—O 2.02 \leftrightarrow 2.06 \rightarrow 2.04 |
| Category B: Add a center of symmetry | | | | | | | | |
| 19 ^r | KENBIO | C ₁₅ N ₃ O ₁₂ Re ₃ | <i>P</i> <i>n</i> a2 ₁ | <i>P</i> <i>n</i> <i>m</i> <i>a</i> | 1 | <i>m</i> | 10 \leftrightarrow 245 | C=O 1.02 \leftrightarrow 1.38 \rightarrow 1.18 |
| 20 ^s | NUYGAP | C ₁₀ H ₇ N ₃ S ₂ | <i>P</i> 2 ₁ | <i>P</i> 2 ₁ / <i>m</i> | 1 | <i>m</i> | 35 \leftrightarrow 98 | C—C 1.34 \leftrightarrow 1.42 \rightarrow 1.38 |
| 21 ^t | QOXPOI | C ₂ Cl ₄ O ₂ Pt ₂ | <i>P</i> 4 ₂ | <i>P</i> 4 ₂ / <i>m</i> | 2 | 2/ <i>m</i> | 0 \leftrightarrow 176 | C=O 1.074 \leftrightarrow 1.080 \rightarrow 1.074 |
| 22 ^u | SEYJAH | C ₇ H ₉ NO ₂ | <i>P</i> 2 ₁ | <i>P</i> 2 ₁ / <i>m</i> | 1 | 2/ <i>m</i> ‡ | 0 \leftrightarrow 152 | — |
| 23 ^v | XIHBOF | C ₃₈ H ₃₃ Cl ₂ N ₂ P ₂ ReS ₂ | <i>C</i> <i>c</i> | <i>C</i> 2/ <i>c</i> | 1 | 2‡ | 27 \leftrightarrow 480 | Re—Cl 2.312§ \leftrightarrow 2.423 \rightarrow 2.423 |
| 24 ^w | ZEQSOD01 | C ₃₄ H ₂₈ FeP ₂ S ₂ | <i>C</i> <i>c</i> | <i>C</i> 2/ <i>c</i> | 1 | $\bar{1}$ | 4 \leftrightarrow 60¶ | — |
| 25 ^x | ZUXBUP | [(η^6 -C ₆ H ₆) ₂ Cr] ⁺ · [OH] ⁻ ·3H ₂ O | <i>A</i> b <i>a</i> 2 | <i>C</i> <i>m</i> <i>c</i> <i>a</i> | 2 | 2/ <i>m</i> | 40 \leftrightarrow 72 | Cr—C 2.103 \leftrightarrow 2.182 \rightarrow 2.142 |
| Category C: Change in Laue group and add a center of symmetry | | | | | | | | |
| 26 ^y | GEWLEZ | C ₁₂ H ₂₃ Cl ₃ NP ₂ Re | <i>P</i> 2 ₁ | <i>C</i> <i>m</i> <i>c</i> <i>m</i> | 1 | <i>m</i> 2 <i>m</i> | 24 \leftrightarrow 187 | C—C 1.22 \leftrightarrow 1.60 \rightarrow 1.38 |
| 27 ^z | YAXKOX | (C ₈ H ₁₂) ₃ C ₄ H ₄ HIr ₃ | <i>P</i> 2 ₁ | <i>C</i> <i>m</i> <i>c</i> <i>m</i> | 1 | <i>m</i> 2 <i>m</i> | 15 \leftrightarrow 190 | C—C 1.48 \leftrightarrow 1.72 \rightarrow 1.54 |
| Category D: Add a center of symmetry and systematic absences | | | | | | | | |
| 28 ^{aa} | KIRWAJ | C ₄₆ H ₃₄ ·2CHCl ₃ | <i>P</i> 2 ₁ | <i>P</i> 2 ₁ / <i>n</i> | 1 | $\bar{1}$ | 5 \leftrightarrow 45 | C—C 1.35 \leftrightarrow 1.43 \rightarrow 1.39 |

Table 1 (continued)

| Number | Refcode | Formula unit | Original space group | Revised space group | Original crystallographically imposed molecular symmetry | Revised crystallographically imposed molecular symmetry | Atomic shifts ($\times 10^3 \text{ \AA}$) min \leftrightarrow max | TMD (\AA) |
|------------------|---------|--|------------------------------------|----------------------|--|---|--|---|
| 29 ^{bb} | WACSAU | $[\text{C}_{18}\text{H}_{18}\text{N}_6\text{Te}]^+ \cdot [\text{TeO}_4]^-$ | <i>Pna</i> 2 ₁ | <i>Pnna</i> | 1 | 2 | 25 \leftrightarrow 118 | C–C 1.32 \leftrightarrow 1.48 \rightarrow 1.40 |
| 30 ^{cc} | QUJXEY | $(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{PdCl}_2$ | <i>P</i> 2 ₁ / <i>c</i> | <i>C</i> 2/ <i>m</i> | 1 | 2/ <i>m</i> | 100 \leftrightarrow 220 | – |

Category E: Add systematic absences

30^{cc} QUJXEY $(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{PdCl}_2$

*P*2₁/*c* *C*2/*m*

1 2/*m*

100 \leftrightarrow 220

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References: (a) Chattopadhyay & Mak (2000); (b) Iitaka *et al.* (1974); (c) Yamazaki *et al.* (1982); (d) Arain *et al.* (1985); (e) Bernardo *et al.* (1999); (f) Cole & Holt (1987); (g) Rasmussen *et al.* (1988); (h) Haasbroek *et al.* (1998); (i) Bera *et al.* (1998); (j) Singh *et al.* (1997); (k) Luna *et al.* (1992); (l) Dell'Amico *et al.* (1994); (m) Alcazar-Roman *et al.* (2000); (n) Casanova *et al.* (1994); (o) Hauptmann *et al.* (2000); (p) Ponikvar *et al.* (2000); (q) Di Noto *et al.* (1995); (r) Calderazzo *et al.* (1989); (s) Ettore *et al.* (1998); (t) Bagnoli *et al.* (2001); (u) Bandoli *et al.* (1989); (v) Mévellec *et al.* (2002); (w) Pilloni *et al.* (1997); (x) Braga *et al.* (1996, 1997); (y) Park *et al.* (1995); (z) Müller *et al.* (1993); (aa) Toyota *et al.* (2000); (bb) Gerber *et al.* (1992); (cc) Casellato *et al.* (1999). † Shifts defined as the min \leftrightarrow max distances from the mean plane of the most populated residue. ‡ Considering the molecular disorder. § The distance 2.312 was eliminated as being unrealistic. ¶ Data determined in comparison with the structure of ZEQSOD published correctly as *C*2/*c* (No. 15) 2 years before ZEQSOD01 (Fang *et al.*, 1995).

The new space group reveals that the two purportedly independent molecules are related by a twofold axis along *b* (the old triclinic *a* axis). The Re^V ion is at the Wyckoff position 4(*a*), while the P atom is at 4(*d*). The reflection condition (in *P*1) *0kl* which is absent for *k* + *l* = odd was not recognized. We have checked this by using 4992 *F*_o values obtained from *Inorg. Chem.* There are 240 *0kl* reflections with *k* + *l* = odd. They are all very weak with *F*_o < 3σ(*F*_o) [only eight reflections have 3σ(*F*_o) < *F*_o < 5σ(*F*_o)], but this is due to the unreasonably small value of σ(*F*_o) rather than to the (small) value of *F*_o. The 4752 reflections were merged according to the Laue symmetry 2/*m*, giving 2500 *F*_o values with an *R*(int) value of 0.065 on *F*_o and 0.121 on *I*. The final full-matrix refinement was based on 129 parameters and one restraint (the total sum of the population of the 11 independent disordered F atoms was restrained to be 3.00). The final *R* factor [*R*(*F*)] was 0.077, slightly greater than the [*R*(*F*)] factor (0.063) obtained by the original authors, but now with fewer parameters. Although the molecular geometry is practically unchanged, as happens

when the space-group change involves two centrosymmetric space groups, a clear improvement in the distances must be noted, for example, the two Re–O distances 1.77 and 1.78 Å become 1.75 Å and the four Re–N distances 2.09, 2.12, 2.13 and 2.15 Å become 2.12 and 2.14 Å. The revised distances are in excellent agreement with those found in the analogous compound *trans*-[ReO₂(cyclam)]⁺·Cl[−]·2(BPh₃·H₂O) (Blake *et al.*, 1988).

This complex presents two IR bands at 809 and 776 cm^{−1}. The original authors suggest attributing the two observed absorptions to the single asymmetric stretching of the [ReO₂]⁺ group associated with each one of the two (purportedly) inequivalent sets of molecules. In the light of the recovered twofold axis the original discussion on the IR spectra requires some reconsideration.

3.5. WERBIE: [bis(4-amino-*N*-2-thiazolylbenzenesulfonamide-*N*)dichloromethanol]copper(II), C₁₉H₂₂Cl₂CuN₆O₅S₄ (Casanova *et al.*, 1994).

This structure was reported to be triclinic, space group *P*1̄ (No. 2), *Z* = 2 (in §2 it is reported as *P*1, but the abstract and CSD report *P*1̄). The triclinic cell can be transformed to an *I*-centered monoclinic cell, space group *I*2/*a*, with *a* = 30.123 (13), *b* = 7.564 (6), *c* = 11.044 (6) Å, α = 90.31 (1), β = 91.27 (1), γ = 90.30 (1)°. The transformation matrix is [112], [1̄00], [010]. The new space group reveals that the molecule lies on the twofold axis along *b* and the methanol molecule is disordered about this axis. The relatively large deviation of α and γ angles from 90° might give rise to suspicions about the space-group change, but similar errors have been already discussed (Marsh *et al.*, 2002; Herbstein *et al.*, 2002). However, we have obtained the *F*_o table (Document No. CSD 57014) from the *Fachinformationszentrum* (Karlsruhe). The Miller indices of the 3855 *F*_o reflections were transformed and the intensities averaged according to Laue symmetry 2/*m*, yielding *R*(int) on *I* of 0.073. The final full-matrix least-squares refinement was based on 173 variables for 2077 reflections; the final *R* factor [*R*(*F*)] was 0.054 for all data. The *R* factor obtained by the original authors was 0.056, but for 328 variables. The space group *I*2/*a* requires the additional reflection

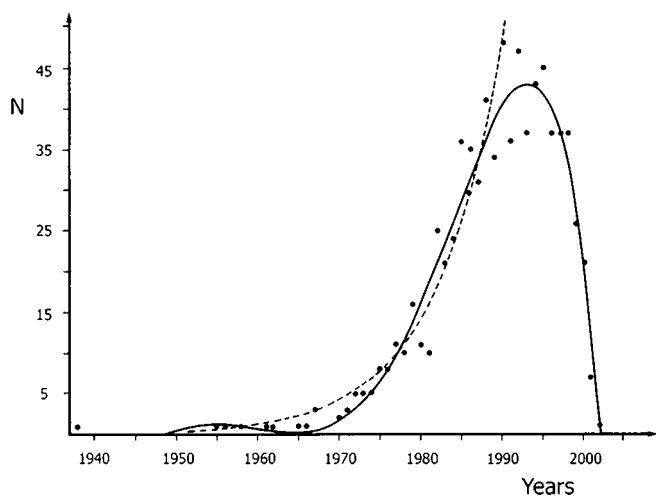


Figure 1
Number of incorrect structures versus publication year. The continuous line was drawn with the least-squares method, while the dotted line is an exponential curve with the equation: $y = 0.0738\exp(0.1224x)$, where $x = (\text{year} - 1937)$.

condition that $h0l$ be absent for $h(l)$ odd. In the original indexing this condition becomes $0kl$ absent for k odd. The reflection list contains only 18 of these reflections, with F_o values ranging from 3.00 to 4.00. Only two reflections, 015 ($F_o = 6.0$) and $0\bar{7}7$ ($F_o = 5.0$), violate this condition (largest $F_o = 184.0$ for $\bar{2}13$). The bond distances undergo very little change.

4. Discussion and conclusions

Category A errors are, as usual, the most numerous, but fortunately they do not produce large distortions of molecular geometry. However, other errors may be introduced with this category, for example, the two IR bands (at 809 and 776 cm^{-1}) in *PAVJUR* were attributed by the original authors to the asymmetric stretching of the two $[\text{ReO}_2]^+$ (purportedly) independent groups, but the space-group change (from $P\bar{1}$ to $I2/a$) reveals that the two purportedly independent molecules are equivalent, being related by a twofold axis. In addition, we have discovered two examples of false polymorphism:

(i) *DAMLIM* was originally described as triclinic ($P\bar{1}$), but then transformed by us to monoclinic ($I2/a$). Three years later, the same authors have described a new polymorph of this compound (*DAMLIM01*) as monoclinic ($C2/c$) without realising that they were dealing with the same crystals;

(ii) a second example is *ABPZCU01* that was reported in the space group $P\bar{1}$, however, the triclinic structure can be transformed to monoclinic $I2/a$.

Twenty-four years before the same compound (*ABPZCU*) was correctly described in the space group $C2/c$. Thus, *ABPZCU01* is not a new polymorph of *ABPZCU*.

We wish to also note that the $P2_1/c$ space group can be incorrectly attributed. In fact, we report three changes (*GULDOG*, *QUJXEY* and *ZOSLIC*) from $P2_1/c$ to more symmetric space groups. This means that all the space groups must be checked before publication or, better still, before dismantling the crystal from the diffractometer.

An interesting example is *ZOSLIC*. Here the space-group change demonstrates that the 2,4 pentanedione moiety is bonded to Mg^{2+} as a neutral ligand, a situation not reported before and not recognized by the original authors (Di Noto *et al.*, 1995). A second interesting example is *QUJXEY* because the change, from $P2_1/c$ (No. 14) to $C2/m$ (No. 12), decreases the number of the space group, but also increases the crystal and molecular symmetry. In fact, $A12/m1$ ($C2/m$, 12) is a minimal non-isomorphic supergroup of $P2_1/c$.

APPENDIX A

One referee has asked us whether the proportion of incorrect structures is static, rising or decreasing. Thus, using various qualifiers as 're-interpretation', 're-determination', 're-refinement', 'correction' *etc.*, we have identified the re-interpreted structures contained in the 5.24 version of the CSD file (703 entries), to which we have added those more recently published (Marsh *et al.*, 2002; Herbststein *et al.*, 2002; Clemente & Marzotto, 2003). Then, 774 incorrect structures resulted.

Fig. 1 shows the number of incorrect structures plotted against the year in which the publication appeared. The plot is exponentially growing up to 1993 and then is quickly decreasing. Such a behaviour is likely due to:

- the time spent between the publication and the correction year;
- the time necessary to update the CSD file;
- the availability of appropriate programs (*MISSYM*, *CHECKCIF*, *PLATON*) to check the space-group correctness. Unfortunately, this analysis lacks nearly 7000 incorrect structures. In fact, Baur & Tillmanns (1986) have evaluated the percentage of possible revisions to be about 3% of all the published structures ($\sim 272\,000$).

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